Maximal entanglement and low-rank approximability by Matrix Product States

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Joint work with Gero Friesecke

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Electronic Schrödinger equation

N-electron Schrödinger equation (PDE in $3N$ dim)

$$H\Psi := \Big(-\tfrac{1}{2}\Delta + \sum_{1\le i<j\le N} \tfrac{1}{|x_i - x_j|} + \sum_{i=1}^{N} v(x_i) \Big) \Psi = E\Psi$$

$\Psi = \Psi(x_1, s_1, \ldots, x_N, s_N) \in L^2_a\big((\mathbb{R}\times\mathbb{Z}_2)^N\big)$

$|\Psi(x_1, s_1, \ldots, x_N, s_N)|^2$ prob. density of electron positions $\in \mathbb{R}^3$ and spins $\in \mathbb{Z}_2$

external potential $v(x) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|x - R_\alpha|}$ encodes chemistry (atom type)

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Curse of dimension

small proteins ($N = 5000$), $\mathbb{R} \to$ 10-grid points $\rightsquigarrow 10^{15000}$ gridpts

Need high accuracy:

Chemmical/biological behaviour $\sim$ energy differences $\ll$ total energies E

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Dream (theory): Find solution manifold which breaks curse of dim

Dream (numerics): efficient algorithm for controlled approximations

Binding energy of N_2

Example (Friesecke, SIAM Talk Slides 2021)

Curse of dimension:

$N = 14$ electrons $\rightsquigarrow$ Schrödinger equation PDE in $\mathbb{R}^{42}$

10 grid-points in each direction $\rightsquigarrow$ 10^{42} gridpoints

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Curse of dimension:
$N = 14$ electrons $\rightsquigarrow$ Schrödinger equation PDE in $\mathbb{R}^{42}$
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Need high accuracy:
basic chemistry (binding) begins in 4th digit of lowest eigenvalue

-109.282174 a.u.	ground state energy (experiment)
-109.282160 a.u.	state of the art simulation (QC-DMRG)
-108.923634 a.u.	energy of two non-bounded nitrogen atoms

Values [WVN14] (similar results [CKG04])

Classical methods: FCI and MCSCF

1. Single-particle space (standard finite Galerkin – choosing orbitals):
$L^2(\mathbb{R}^3 \times \mathbb{Z}_2) \approx \operatorname{span}\{\varphi_1 \dots \varphi_L\}$

2. N-particle space (associated tensor product – FCI space):
$L_a^2\big((\mathbb{R}^3 \times \mathbb{Z}_2)^N\big) \approx \operatorname{span}\left\{\left|\varphi_{i_1} \dots \varphi_{i_N}\right\rangle \,\middle|\, 1 \le i_1 < \dots < i_N \le L\right\} =: \mathcal{V}_{N,L} \quad \dim = \binom{L}{N}$

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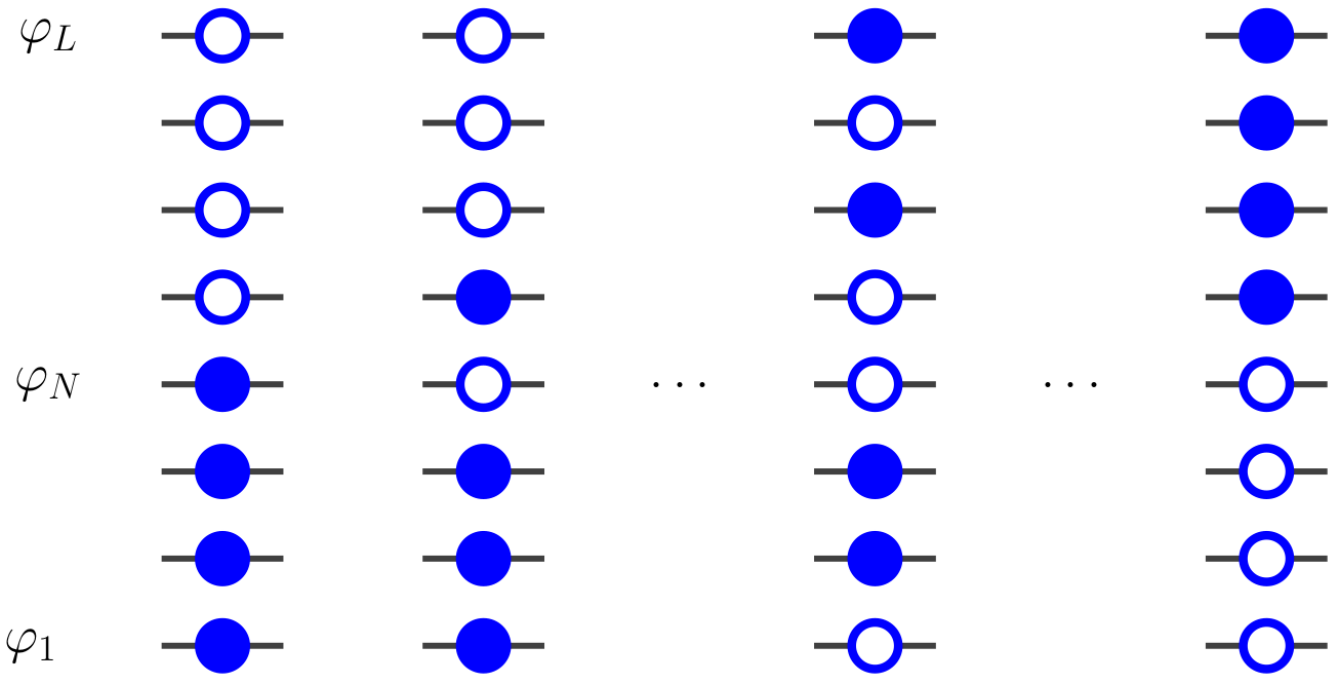

Figure 1: Schematic picture of FCI space

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FCI: Fix orbitals (Hartree-Fock), minimize Rayleigh quotient over expansion coefficients
$\Psi_{\mathrm{FCI}} = \operatorname{argmin}\left\{\frac{\langle\Psi, H\Psi\rangle}{\langle\Psi,\Psi\rangle}\middle|\Psi \in \mathcal{V}_{N,L}\right\}$

MCSCF: Minimize Rayleigh quotient over both orbitals and expansion coefficients
$\Psi_{\mathrm{MSSCF}} = \operatorname{argmin}\left\{\frac{\langle\Psi, H\Psi\rangle}{\langle\Psi,\Psi\rangle}\middle|\Psi \in \mathcal{V}_{N,L}(\varphi_i),\ \varphi_i \in H^1(\mathbb{R}^3), \langle\varphi_i, \varphi_j\rangle = \delta_{ij}\right\}$

Do not break curse of dimension. Unfeasible for computations beyond small number of electrons

Low-rank approximation

3. Low-rank approximation (CP-format – separation of variable):

$$\Psi \approx \sum_{\nu=1}^{M} \left| a_1^{(\nu)} a_2^{(\nu)} \cdots a_N^{(\nu)} \right\rangle, \qquad a_i^{(\nu)} \in \operatorname{span}\{\varphi_1, \ldots, \varphi_L\} \qquad \text{dim} = M \cdot N \cdot L$$

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Positive results

- asypmotically exact with small M for atomic ions with large nuclear charge [FG10]
- small error for $Lu = f$ with smooth f in high dimension [DDGS16]

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Did not work well in practice

- Need a ton of terms Kato [Kat57]

  Eigenstates of Schrödinger equ. **nonsmooth** $\Psi \sim |x_i - x_j|$ $(x_i \to x_j)$
- Too hard to compute Hillar, Lim [HL13]

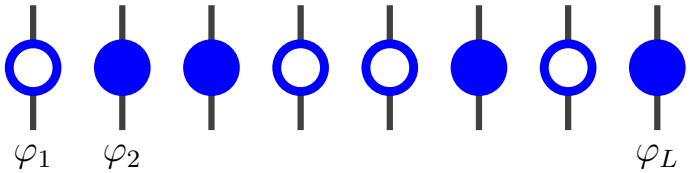
  "Most tensor problems are NP-hard"
- Approximation manifold not closed for $N \geq 3$ DeSilva, Lim [DSL08]

  "Tensor rank and ill-posedness of the best low-rank approximation problem"

QC-DMRG – Definitions

1. Occupation representation (Fock space point of view)

$$|\varphi_2\varphi_3\varphi_6\varphi_8\rangle \longleftrightarrow \Phi_{01100101},$$



$$\Psi = \sum_{\mu_1,\ldots,\mu_L=0}^{1} C_{\mu_1,\ldots,\mu_L}\Phi_{\mu_1,\ldots,\mu_L}$$

$$\text{dim} = 2^L = \sum_{N=0} \binom{L}{N}$$

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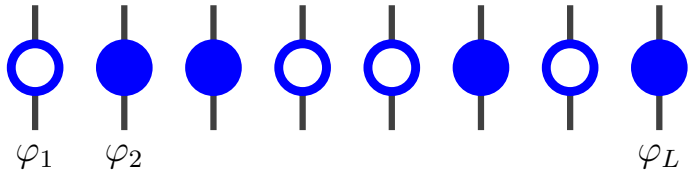

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2. **Matrix product states/ tensor-trains**

$$C_{\mu_1,\ldots,\mu_L} \approx \sum_{\alpha_1,\ldots,\alpha_{L-1}=1}^{M} \underbrace{A_1[\mu_1]_{\alpha_1}}_{1\times M}\underbrace{A_2[\mu_2]_{\alpha_1,\alpha_2}}_{M\times M}\cdots\underbrace{A_L[\mu_L]_{\alpha_{L-1}}}_{M\times 1} \qquad \text{dim} = L\cdot M^2\cdot 2$$

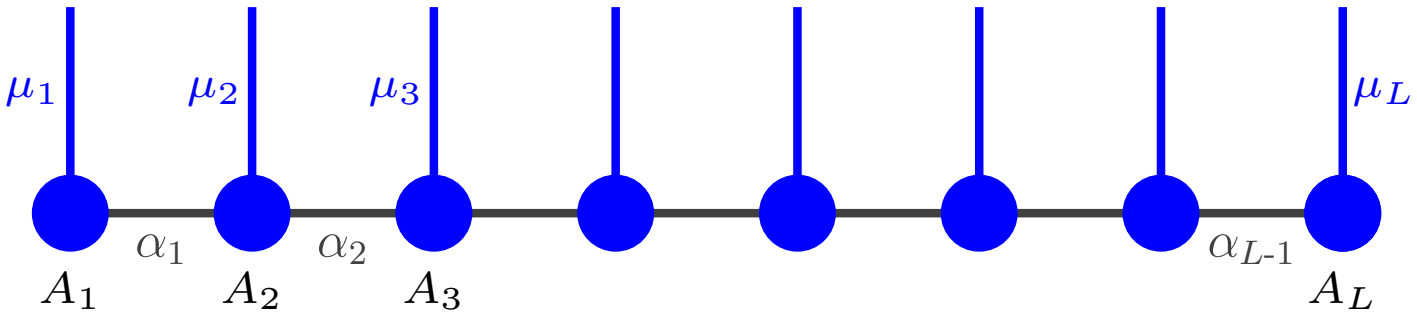

Figure 1: μ_i physical variables (occupation); α_i virtual variables (contracted)

QC-DMRG – Properties

- Minimize Rayleigh quotient over QC-DMRG ansatz
  standard algorithm: DMRG (origin:spin chains), hence name of method
- Truncate each A_j via SVD to a reasonable size M ($M \approx 2000 - 5000$)
  Theory: ansatz exact for $M \geq \max_{k=1,\ldots,L-1} \operatorname{rank} C^{\mu_1 \cdots \mu_k}_{\mu_{k+1} \cdots \mu_L}$
- Parameter M interpolates between HF and FCI
  HF: $M = 1$, FCI: $M = 2^{L/2}$
- Format approximates solutions to el. Schrödinger eq. well for moderate M
  depends on choice of underlying tensor network
- Approximation manifold closed
  if network has **no** loops

good reviews: Schollwoeck [Sch11] MPS, Szalay et al. [SPM+15] QC-DMRG

Choosing the network

Within the tensor-train format and for fixed orbitals, the fundamental issue of choosing the network boils down to choosing the ordering.

Figure 2: Schematic picture of a MPS before and after reordering the orbitals

Orderings matter

Fermionic Bell states: example with $L = 2N$ [GF21]

$\left| \frac{\varphi_1+\varphi_{N+1}}{\sqrt{2}} \frac{\varphi_2+\varphi_{N+2}}{\sqrt{2}} \dots \frac{\varphi_N+\varphi_{2N}}{\sqrt{2}} \right\rangle$ requires bond-dimension 2^N

New ordering $\varphi_1, \varphi_{N+1}, \varphi_2, \varphi_{N+2}, \dots \rightsquigarrow$ bond-dimension 2

Current method Fiedler ordering [BLMR11]

concepts from QIT and spectral graph theory

Find permutation that maximizes quantum mutual information

New method BWPO [DF21]

Relies on inversion symmetry for singular values of Slater determinants

tailored to Quantum Chemistry

How can we gain with optimal orderings?

Maximally entangled state:

$$\Psi_{\mathcal{P}} = \sum_{i_1<\ldots<i_N} \lambda_{i_1,\ldots,i_N} |\varphi_{i_1} \ldots \varphi_{i_N}\rangle$$

coefficients $\lambda_{i_1,\ldots,i_N}$ are mutually different elements of $\mathcal{P} = \{\sqrt{p_j} : p_j \text{ prime}\}$

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Theorem (Max. entangled MPS [GF21])

States of the type $\Psi_{\mathcal{P}}$ require in every step the maximal bond-dim of $\min\{2^j, 2^{L-j}\}$ ***regardless*** *of the chosen ordering.*

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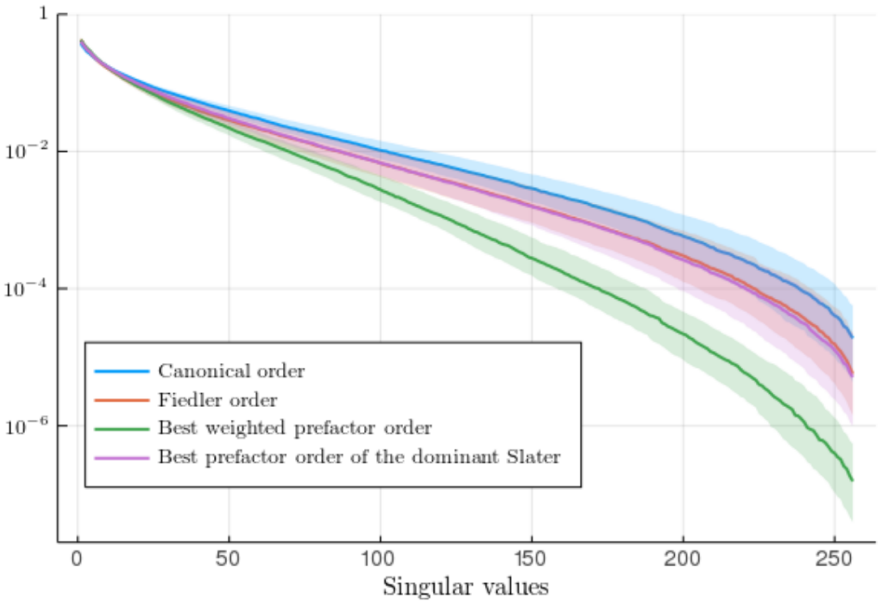

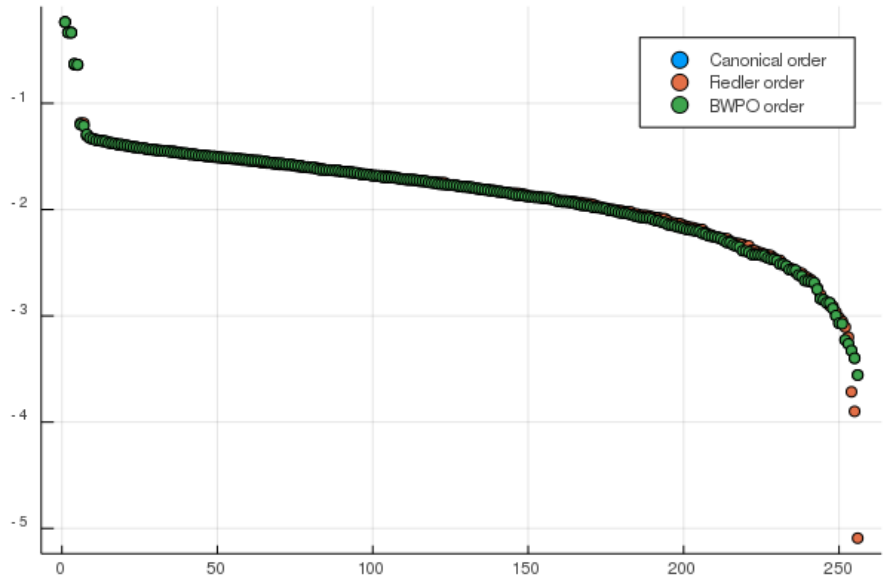

Figure 3: Singular values of $C^{\mu_1\ldots\mu_{L/2}}_{\mu_{L/2+1}\ldots\mu_L}$, $N = 8, L = 16$;
left sum of 2 Slaters wights 0.9 and 0.1 (mean solid, ribbon 0.75 quantile) [DF21];
right max. entangled state $\Psi_{\mathcal{P}}$ [GF21]

Unitary transformations instead of orderings

Arbitrary fermionic mode transformations: [FG21]
single-particle reduced density matrix $\gamma_\Psi : \mathcal{H}_L \to \mathcal{H}_L$ defined by

$$\langle \Psi,\, a^\dagger(\varphi_i) a(\varphi_j) \Psi \rangle = \langle \varphi_j,\, \gamma_\Psi \varphi_i \rangle \quad \text{for all } i, j.$$

Expand Ψ in eigenbasis of γ_Ψ (natural orbitals) [CY00]:

In two-particle case ($N = 2$), this gives nice structure
$\rightsquigarrow$ find explicit matrices such that max. bond-dim ≤ 3

lower bound guarantees bond-dim. 3 necessary
(analyze structure of general unfoldings)

Complete characterization in the Two-particle case

Theorem (Characterization Two-particle case [FG21])

Suppose $L \geq 4$ even, $\Psi \in \mathcal{V}_{2,L}$, and γ_Ψ has maximal rank $= L$.
Then, for any basis $\{\varphi_1, ..., \varphi_L\}$ and any MPS-representation with bond dimensions $(r_1, \ldots, r_{L-1})$ we have

- *$r_j \geq 2$ for every $j \in \{1, \ldots, L-1\}$*
- *At least one of two consecutive elements (r_j, r_{j+1}) for $j \in \{2, \ldots, L-2\}$ is at least 3.*

$(r_1, ..., r_{L-1})$ with lowest ℓ^1-norm is $(2, \underbrace{2, 3, \ldots, 2, 3}_{L-4 \text{ times}}, 2, 2)$

Corollary

For two-electron systems, QC-DMRG with optimal fermionic mode transformation is exact for bond-dim $M = 3$.

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The results also hold for the full two-electron Hilbert space $L^2_a\big((\mathbb{R}^3 \times \mathbb{Z}_2)^2\big)$, in which case an MPS of bond-dim M is a half-infinite chain of $M \times M$ matrices.

Summary & open problems

- tensor network methods are fast becoming one state-of-art method (system sizes up to 50 electrons)
  theory still lacking $\rightsquigarrow$ optimizing network promising direction

- Questions concerning orderings
  - How rare are states like $\Psi_{\mathcal{P}}$? Results about average states?
  - Are there states with SVs independent of re-ordering?
  - Improved result about certain class of states (GS of nice Hamiltonian)?

- Unitary transformations useful in practice? (more expansive!)

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Thank you very much for your attention!

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